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PROJECT B-366

ATMOSPHERIC CONTAMINATION AND TRIBO ELECTRIFICATION

EDWARD E. WEAVER AND CLYDE ORR, JR.

Research Grant AP00741-02

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Tribo electrification between various substrates and platinum was investigated with a number of gases, vapors, and gas mixtures present in order to determine the effects of humidity and gaseous pollution and to investigate the mechanisms of frictional charging. The substrates were formed into discs and rotated against platinum in a chamber which could be evacuated and filled with any gas or gas mixture at pressures up to atmospheric over a range of temperatures. Results confirmed that in pure air, water vapor exerts a predominant influence on electrostatic charging and suggested that a maximum occurs in the generated voltage conditions such that a layer of adsorbed water a very few molecules thick was present. Other experiments indicated that, in the presence of air, most pollutant gases had only a slight effect on the voltage generated. In the presence of air, no gases were found that caused an increase in tribo electrification.

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I. SUMMARY

Tribo electrification between various substrates and platinum was investigated with a number of gases, vapors, and gas mixtures present in order to determine the effects of humidity and gaseous pollution and to investigate the mechanisms of frictional charging. The substrates were formed into discs and rotated against platinum in a chamber which could be evacuated and filled with any gas or gas mixture at pressures up to atmospheric over a range of temperatures.

Results confirmed that, in pure air, water vapor exerts a predominant influence on electrostatic charging and suggested that a maximum occurs in the generated voltage under conditions such that a layer of adsorbed (or sorbed) water a very few molecules thick was present. Other experiments indicated that, in the presence of air, most pollutant gases had only a slight effect on the voltage generated. However, HCl vapor reduced the voltage to zero. In the presence of air, no gases were found that caused an increase in tribo electrification. Pollutant gases alone caused little or no charging with most substrates; nylon and silica glass were exceptions, however.

Any of several theories might be applied to the results. These include the contact potential theory; ion transfer caused by disruption of the Stern-Gouy layer; charge separation due to the random breaking of particulate matter from the substrate having an uneven distribution of charges associated with the pieces; chemical reaction between the adsorbed gas and the solid involving frictional catalysis; and piezoelectric generation due to adsorbed-

layer, molecular distortion.

The contact potential theory does not explain the influence of adsorbed gases or the high voltages developed; it undoubtedly contributes in the very low voltage regions. Under evacuation, electrostatic noise was found to be high, suggesting that under this condition random charging might be being generated by the breaking of particulate matter from the substrate. The theory involving a chemical reaction between the gas and the solid is not in direct conflict with any data, however the responses of charge vs. humidity, charge vs. partial pressure of water vapor, and charge vs. temperature would be expected to be different if the cause of charging were chemical in nature.

Piezoelectric generation of charges due to the forces applied on adsorbed, dielectric molecules and their resulting distortion is probably the most significant source of charging under low surface coverage conditions. Current concepts of adsorbed (or sorbed) molecular species indicate that the first layer or so of such attached molecules should have an appropriate ordered structure. Disruption and distortion within the Stern-Gouy layer possibly contributes to tribo electrifications as adsorbed (or sorbed) gases and vapors build to depths of several molecular layers.

II. INTRODUCTION

Friction between certain substances, e.g., wool and hard rubber, silk and glass, paper and plastic, is well known as a producer of electrostatic charging. Atmospheric humidity is also generally recognized to exert a significant influence on the magnitude of the charging. Not known, however, are the effects on electrostatic charging of vapors and gases that are now in the atmosphere as pollutants. The objective of this work was to determine the effects of such vapors and gases and to investigate the mechanisms involved in electrostatic charging.

Static electrification encompasses all processes that produce a segregation of positive and negative electrical charges by mechanical action through (1) contact, friction, or impact between solid surfaces and between solid and liquid surfaces, and (2) rupture or separation of surfaces, including solid from solid, liquid from solid, and gas from solid. The details of the processes are not completely understood even though a number of basic mechanisms have been described.

The first mechanism is identified as contact potential. Metals exhibit varying electron energy levels within their structure, and electron transfer occurs when two, dry, dissimilar metals, or a metal and a semiconductor, are brought into contact. Separation then results in the creation of net charges. The second mechanism involves ion transfer. Dielectric liquids intrinsically exhibit an electrical double layer (the Stern-Gouy layer) at an interface. The interface may be between a liquid and a solid or between a liquid and a gas. As a consequence, disruption of such a liquid interface either by spraying or by flowing over a solid gives rise to charge

separation. The third is homogeneous or symmetrical charge separation as a result of statistically random fluctuations of charges within a body and, specifically, on the two sides of a boundary at the time of rupture. This mechanism of charging comes into being when relatively small solid particles are separated from one another or from massive portions of the same matter. The fourth mechanism involves ions or electrons in gases, especially in flames, in contact with solids that are segregated mechanically by mass motion of the gases relative to the solids. The fifth is revealed by crystals in which mechanical forces alter polarization, i.e., the piezo-electric distortion. So-called frictional, or tribo, electrification may involve several of the mechanisms outlined at the same time.

This study has involved measurements of charging under carefully controlled conditions with friction created mechanically. The friction was developed between substances having reproducible compositions in the presence of various gases and vapors and mixtures of gases and vapors.

III. APPARATUS AND MATERIALS

The apparatus employed to investigate frictional electricity in this study evolved through a series of designs, attaining the form described below for most of the study. The central, mechanical component was mounted on the bottom of a non-magnetic, stainless steel tank. A bell jar inside the tank covered the central unit of the apparatus so that it could be evacuated. The space between the bell jar and the tank walls was filled with a liquid for temperature control purposes. Temperatures could be maintained from - 131°C to 150°C.

The system within the bell jar consisted of a sample holding disc 3 inches in diameter mounted horizontally on a vertical shaft. Both ends of this shaft were supported by needle bearings. Magnets were mounted to the shaft below the sample disc, these magnets coupling through the tank bottom with opposing magnets mounted to an external drive motor. This system permitted rotary motion while maintaining a vacuum. A rotation rate of either 1200 or 180 rpm was employed in the tests. A platinum piece rested on the sample which, in turn, was mounted on the holding disc. The platinum piece was held in place by a guide that permitted it to "float" on any sample substrate attached to the rotating mechanism. Actually, it pressed on the substrate with a force of 1.64 gm/cm^2. Electricity developed due to friction was conducted from the platinum through the guide and a high vacuum insulator to a Keithley, Model 610A, electrometer. The input resistance of the electrometer was 10^{14} ohms. When a Keithley, Model 6103A, 1000:1 divider probe was employed this resistance dropped to 10^{11} ohms.

Various gases were admitted to the system by means of a manifold using bellows valves. The manifold also cornected the bell jar to a vacuum system consisting of a roughing pump, two-stage oil diffusion pump, and a cold trap. Pressure measurements were made using a manometer filled with Dow Corning 705 fluid and a Numinco, Model MIC-401, thermistor pressure gauge. Measurements were taken with the manometer using a cathetometer. Figure 1 is a photograph of the apparatus and associated equipment. Figure 2 is a schematic diagram of the charging apparatus.

Ancillary equipment included a Cambridge Systems, Model 880, dewpoint hygrometer for measuring the humidity of the air. A Honeywell electronic voltmeter, Model 333, was used in conjunction with thermistors to measure the temperature inside the bell jar and in the bath. The outputs of both the electrometer and the hygrometer were monitored with a Moseley, Model 17500A, double-pen recorder.

Solid materials examined for frictional charging behavior included cellulose, felt, graphite, mica, nylon, polyethylene, polytetrafluroethylene, rubber, selenium, silica (glass), silica (fused), sodium chloride, stearic acid, and sulfur. For purposes of standardization, the opposing frictional material was always platinum.

The nylon, polyethylene, and polytetrafluroethylene were obtained as pure plastics containing no dyes or coloring agents. The cellulose was high-purity, ashless filter paper. The graphite was a high purity grade. The slip used to prepare fused silica pieces was of the quality normally used to make ablative nose cones. Sodium chloride, stearic acid, and sulfur, were hot pressed into solid forms using a polished, stainless steel die with a 50-ton hydraulic press. Fused silica pieces were prepared from

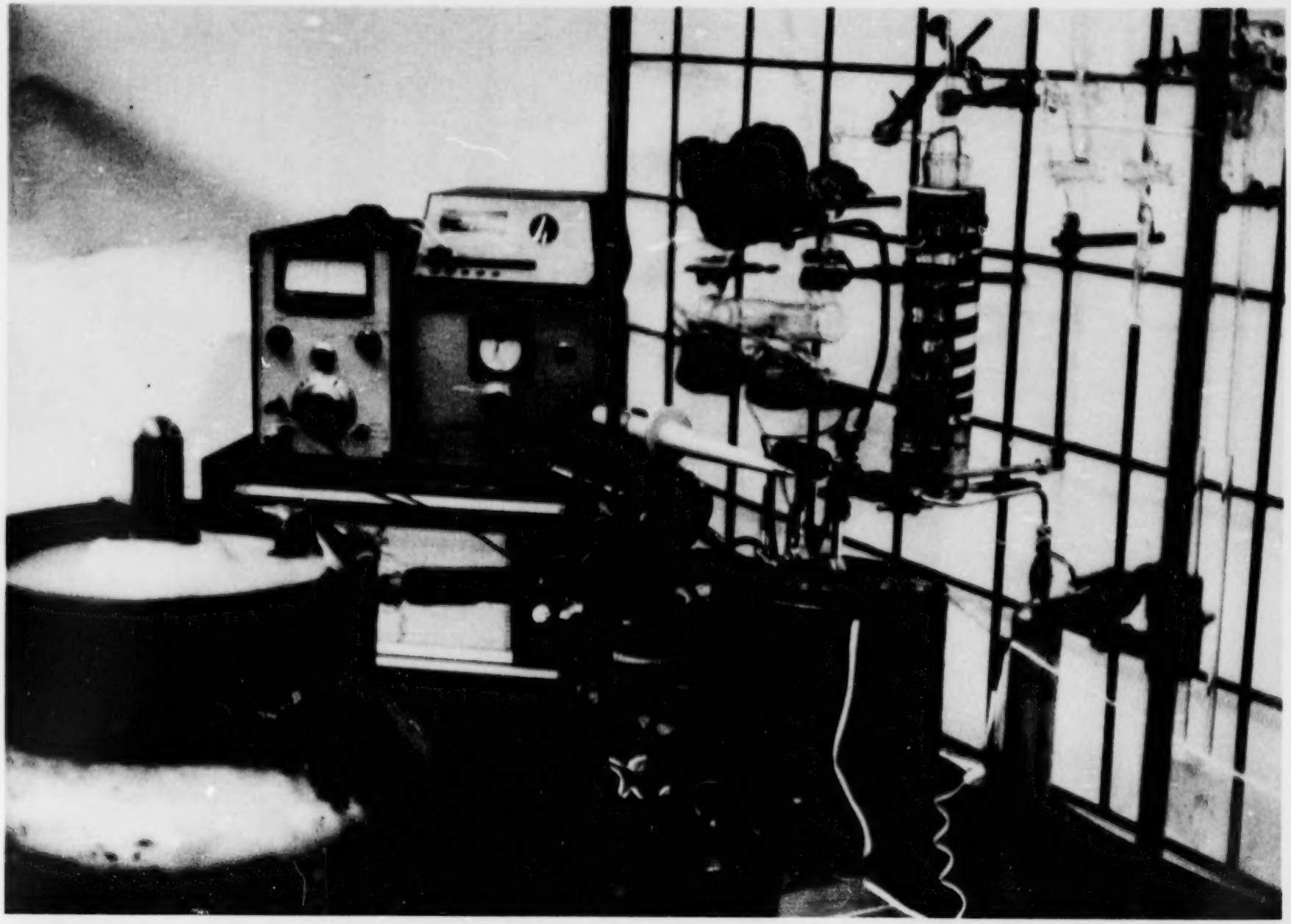

Figure 1. Electrostatic Charging Apparatus, Vacuum System, and Electronic and Temperature Control Equipment.

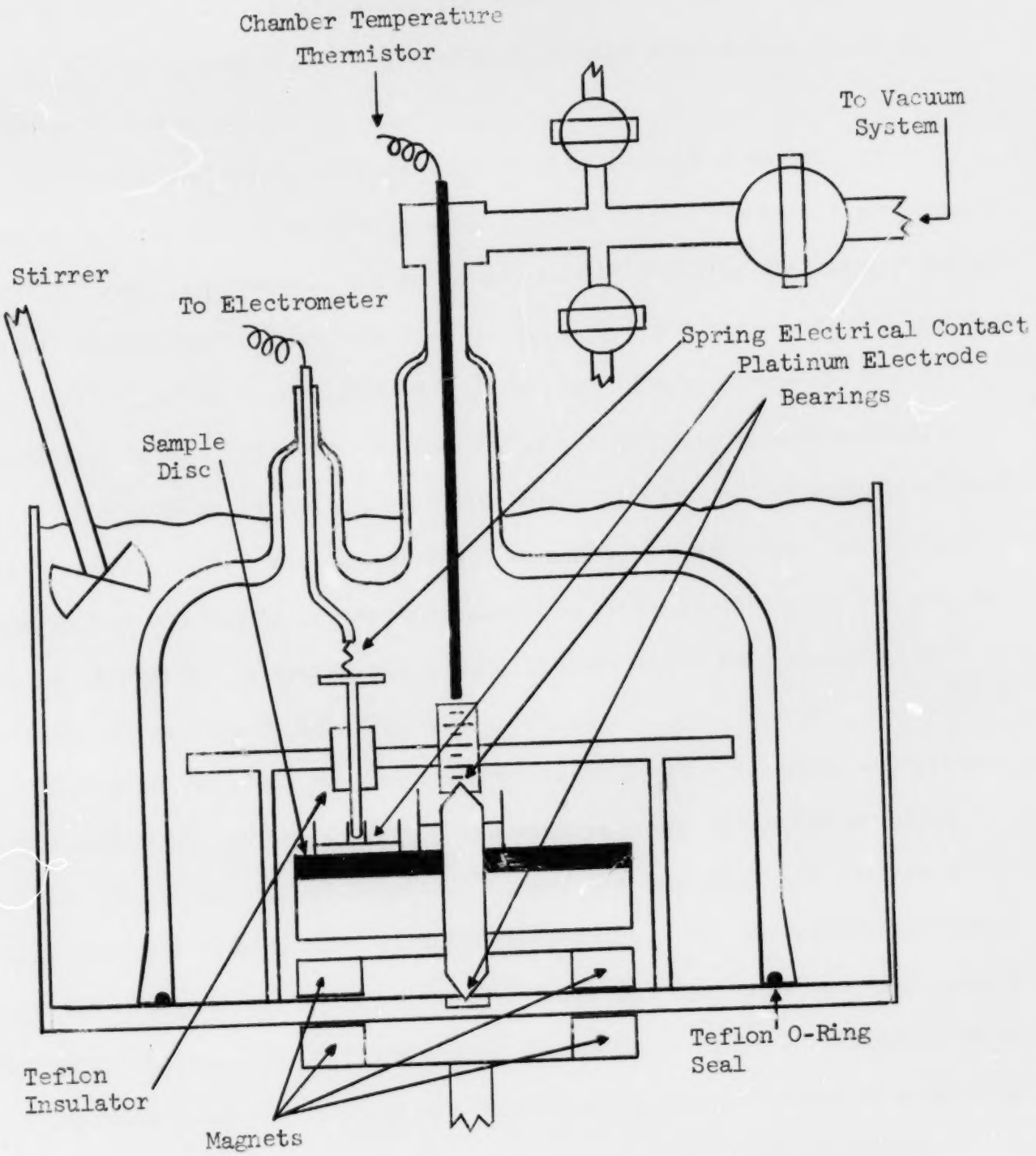

Figure 2. Schematic Diagram of Charging Apparatus

slip cast in a suitable mold. The pieces were removed from the mold and fired at 1100°C. The stearic acid was melted and molded to the proper shape. All other materials were either purchased with, or machined to, the desired shape.

Machinable materials were reduced to size (3-inch diameter) and given a flat surface by machining with a clean carbon steel tool and placed directly in the apparatus. The machined face of the disc was never touched. Pressed samples were taken from the die while hot and placed in the apparatus. Silica pieces were washed with laboratory-grade detergent, rinsed, etched with dilute hydrofluoric acid solution, and rinsed with distilled water. The samples of cellulose, felt, and mica were washed with detergent, rinsed with distilled water, and dryed in a hot, vacuum oven. Each time a new sample was placed in the apparatus the platinum electrode was polished on a metallurgical polishing wheel with diamond abrasives, rinsed with distilled water, and dryed in a vacuum oven.

Glycerine was added to the temperature bath after a sample was placed in the apparatus. A heater with thermostat was then activated to bring the bath temperature to at least 100°C, and the apparatus and samples were "outgassed" for several days at this temperature. The thermistor pressure gauge did not indicate below about 10^{-4} torr, and this pressure was usually attained within the first few hours of evacuation. Later measurements with an ionization gauge showed that the system was readily capable of attaining 5×10^{-6} torr, so evacuation to near this pressure was probably always achieved. The thermistor pressure gauge was mounted so that the indicated pressure would be the true pressure inside the bell jar. The lines to the gas cylinders were also evacuated for extended periods to remove as much

contamination as possible from them.

Swagelok fittings with Teflon ferrules were employed in making connections except at the top of the bell jar; here ground-glass joints were used. A Teflon O-Ring completed the seal at the bottom of the bell jar. The top needle bearing surface was Teflon, but brass lubricated with molybdenum disulfite was necessary for the lower one in order to support the weight of the rotating system and magnetic thrust or it.

IV. EXPERIMENTAL RESULTS

The following experiments were performed with the apparatus and solid substrates described above. They included measurements of electrostatic charging as a function of relative humidity, electromagnetic radiation, gas composition in air, water vapor at various pressures, temperature, and gases at various pressures and temperatures.

A. Electrostatic Charging as a Function of Humidity

First studies involved electrostatic charging as a function of relative humidity, since humidity was known to be a factor of much significance. Air supposedly devoid of hydrocarbons and of very low moisture content was employed initially. Before introduction into the system, the air stream was divided into two parts, one bubbling through distilled water and one passing directly into the apparatus. The ratio of dry and moist air, hence the relative humidity, was controlled by regulating the two flow rates. The dew point of the stream actually entering the system was measured to an accuracy of about one per cent.

No significant charge at any humidity was developed by friction between platinum and polethylene and polytetrafluroethylene. Mica showed a peak of -1.2 volts at 47 per cent relative humidity and a rotation rate of 1200 rpm. Cellulose produced a maximum of -79 volts at 22 per cent relative humidity and the same rate of rotation; at low humidities the output was slightly negative. Stearic acid produced an essentially constant -0.22 volts from a low humidity to near saturation. Sodium chloride showed a very characteristic charging curve as a function of humidity, generating in excess of 100 volts at a rotational rate of 1200 rpm.

The response with sodium chloride will be discussed in more detail later. All curves were smooth with no sharp changes in slope. The data showed that the generated potential approached zero as the humidity approached either 0 or 100 per cent and that air humidity was, indeed, a significant factor in electrostatic charging under certain circumstances.

B. The Influence of External Radiation on Electrostatic Charging

To determine if the electronic state of the surface atoms of the material undergoing friction had any influence on charging, a sample of selenium was tested with a rotational rate of 1200 rpm. Following evacuation, the area of the sample just ahead of the platinum wiper and just prior to its moving under the wiper was exposed to darkness, room light, a 20 watt unfiltered mercury vapor lamp, a pair of 20 watt ultraviolet lamps, and the beam of a 5 milliwatt helium-neon laser. Under all of these conditions the electrostatic charging remained low and unaltered.

C. The Effect of Vapors and Gases in the Presence of Air

The influence of other gases and vapors on electrostatic charging was investigated by allowing air of approximately 20 per cent relative humidity to which other gases and vapors were added to pass through the apparatus. The added components included HCl, NH_3, CH_3COCH_3, SO_2, CH_3CH_2OH, and tobacco smoke. With a mica substrate, NH_3 caused a slight decrease in negative charging and cigarette smoke a small increase in the absolute voltage developed. HCl gas caused the generated voltage to decrease from a negative value to zero; when the HCl was removed by evacuation the original voltage was re-established. With cellulose, the addition of NH_3 reversed the polarity, making it charge slightly positive. The addition

of HCl gas decreased the negative charging characteristic of cellulose. With a stearic acid substrate, NH_3, HCl, CH_3CH_2OH, and $CH_3CH_2CH_3$ gases had either a very small effect or no measurable effect on the generated voltage. All of the above tests were made at room temperature, 25 to 27°C, using a rotational rate of 1200 rpm.

It is worthy of note that, in the presence of air, HCl had the strongest influence on all of the substrates. The other gases had either slight influence or no influence at all. In the moderately dry air of these tests, none of the gases caused a significant increase in the absolute voltage.

D. Effects of Water Vapor on Electrostatic Charging

Since water vapor seemed to exert a primary influence, studies were next made with it as the only gas present. Sodium chloride was the first solid to be studied. Data were recorded using a rotational rate of 1200 rpm as open-circuit voltage vs. relative pressure, short-circuit current vs. relative pressure, and power dissipated across a 2.5 megohm resistor vs. relative pressure. A low temperature, nitrogen (B.E.T.) surface area analysis[1] of the compacted sodium chloride piece yielded a specific surface area of 0.22m^2/gm. An H_2O sorption isotherm at 27°F was next determined on the same sample. Using 12.5 $\mathring{A}^2$ as the area occupied by one water molecule when sorbed[2], data were obtained on the average number of water molecule layers as a function of relative pressure. The charging data for the sodium chloride disc were then plotted as a function of the average number of sorbed layers. These data are shown on Figures 3, 4, and 5, respectively. Similar data with a fused silica disc obtained in the same manner are shown in Figures 6, 7, and 8.

Other samples tested with water vapor only present included silica

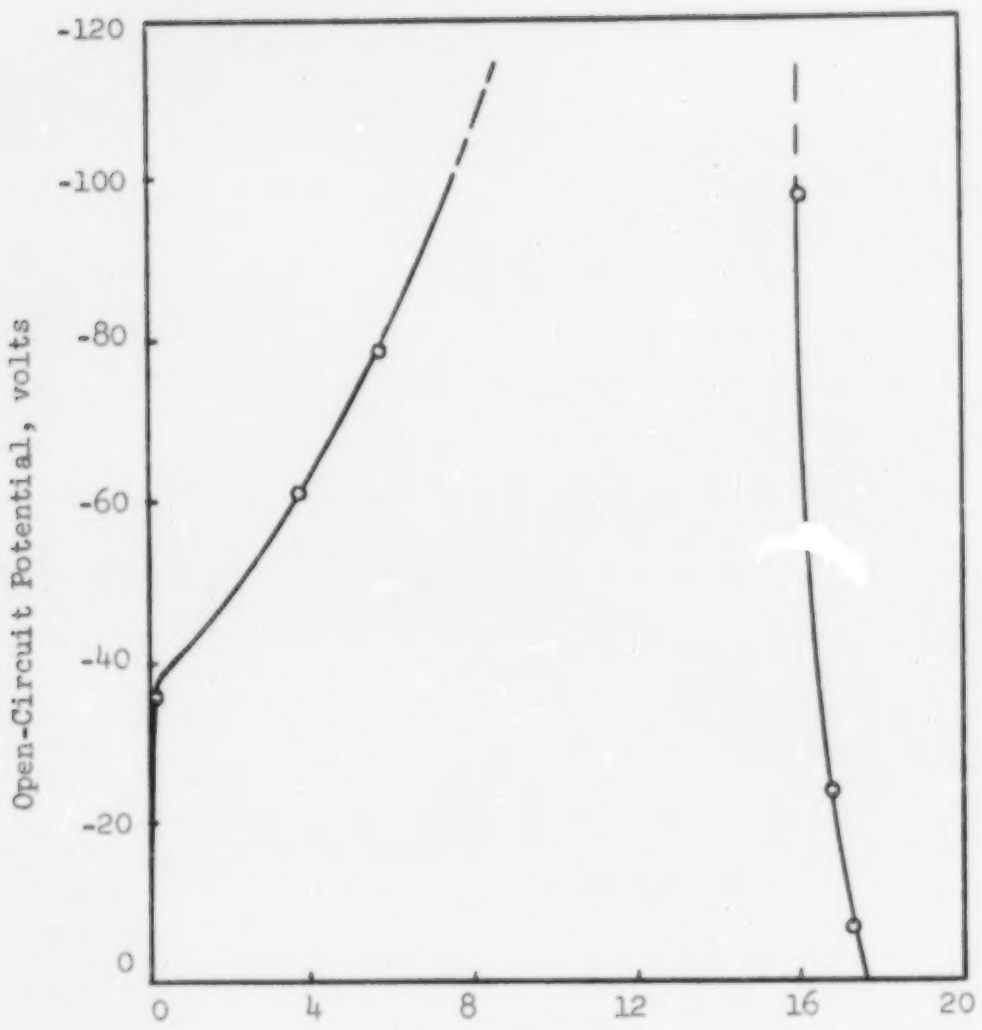

Figure 3. Open-Circuit Potential Generated by Platinum on Sodium Chloride as a Function of Layers of Sorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

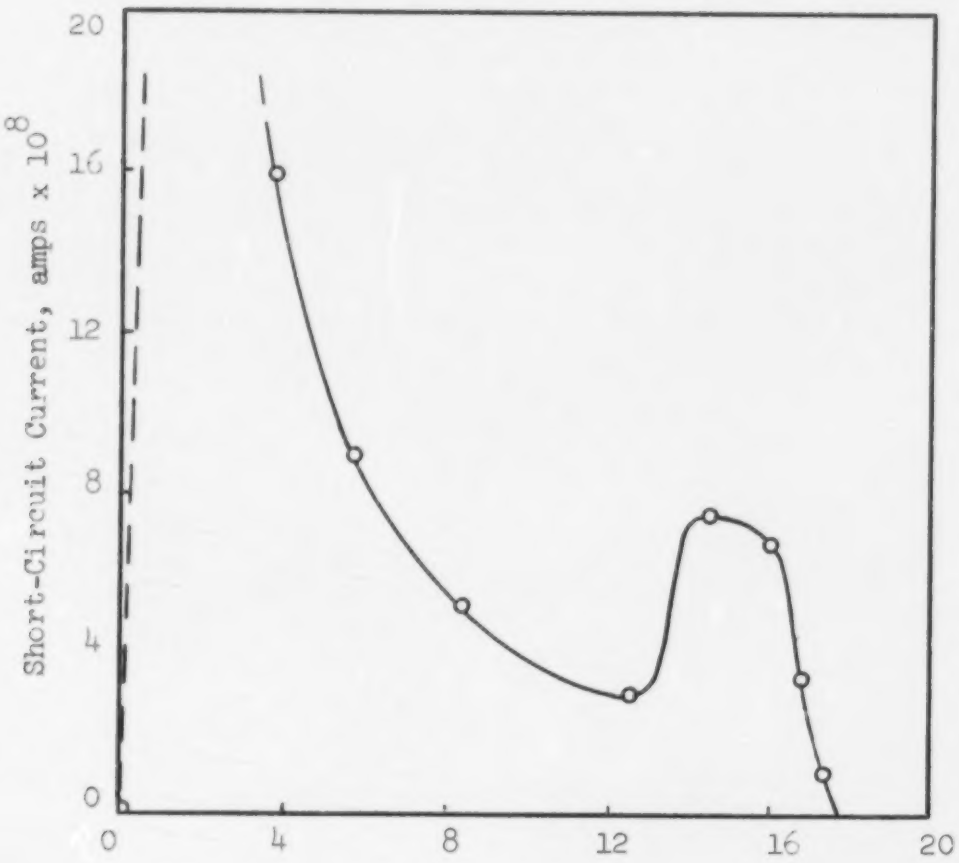

Figure 4. Short-Circuit Current Generated by Platinum on Sodium Chloride as a Function of Layers of Sorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

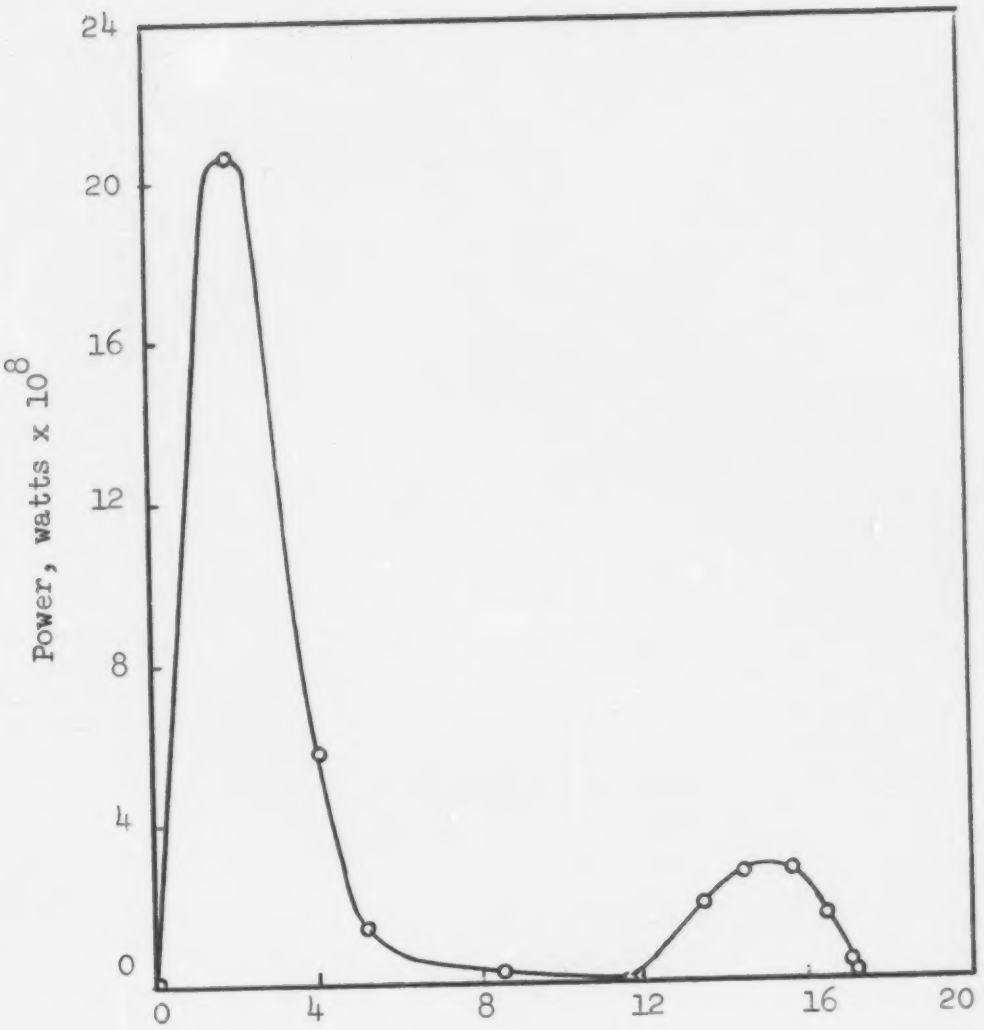

Figure 5. Power Dissipated Across a 2.5×10^6 Ohm Resistance by Platinum on Sodium Chloride as a Function of Layers of Sorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

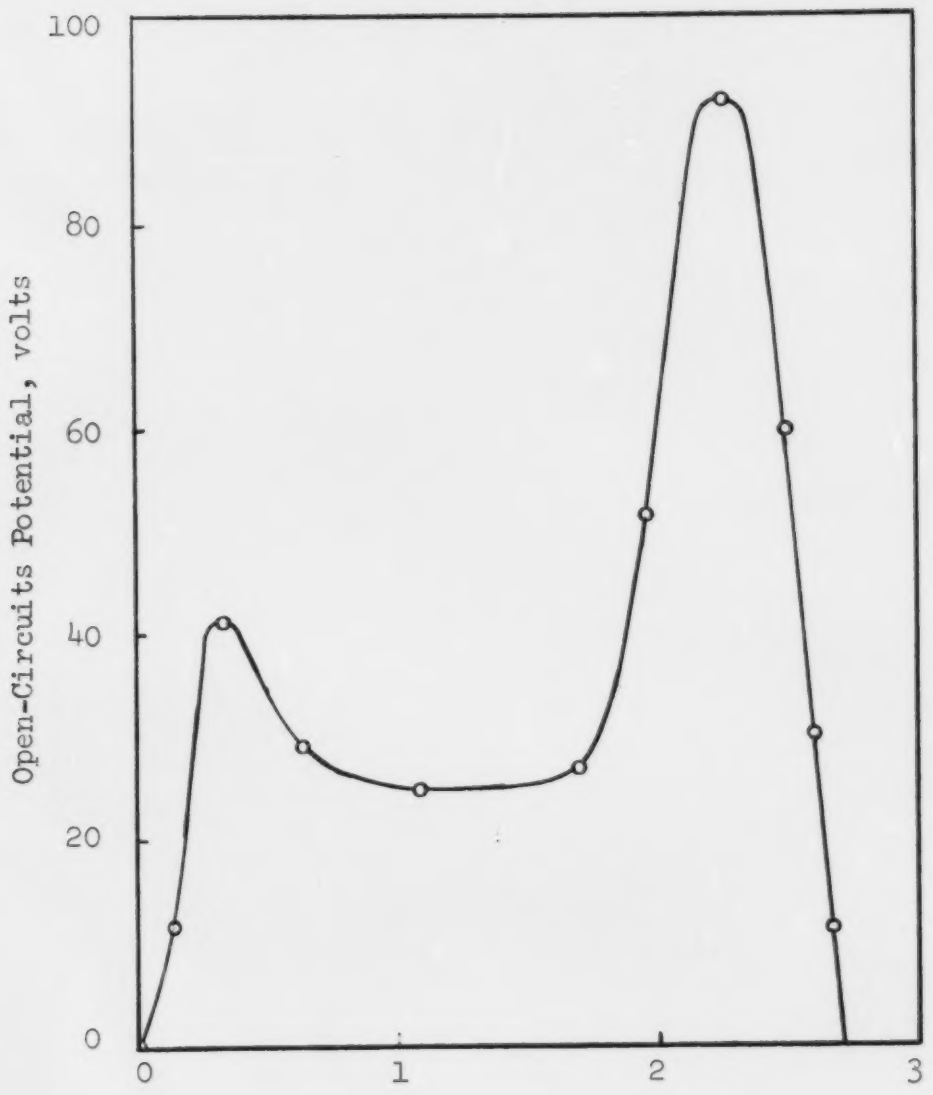

Figure 6. Open-Circuit Potential Generated by Platinum on Fused Silica as a Function of Layers of Adsorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

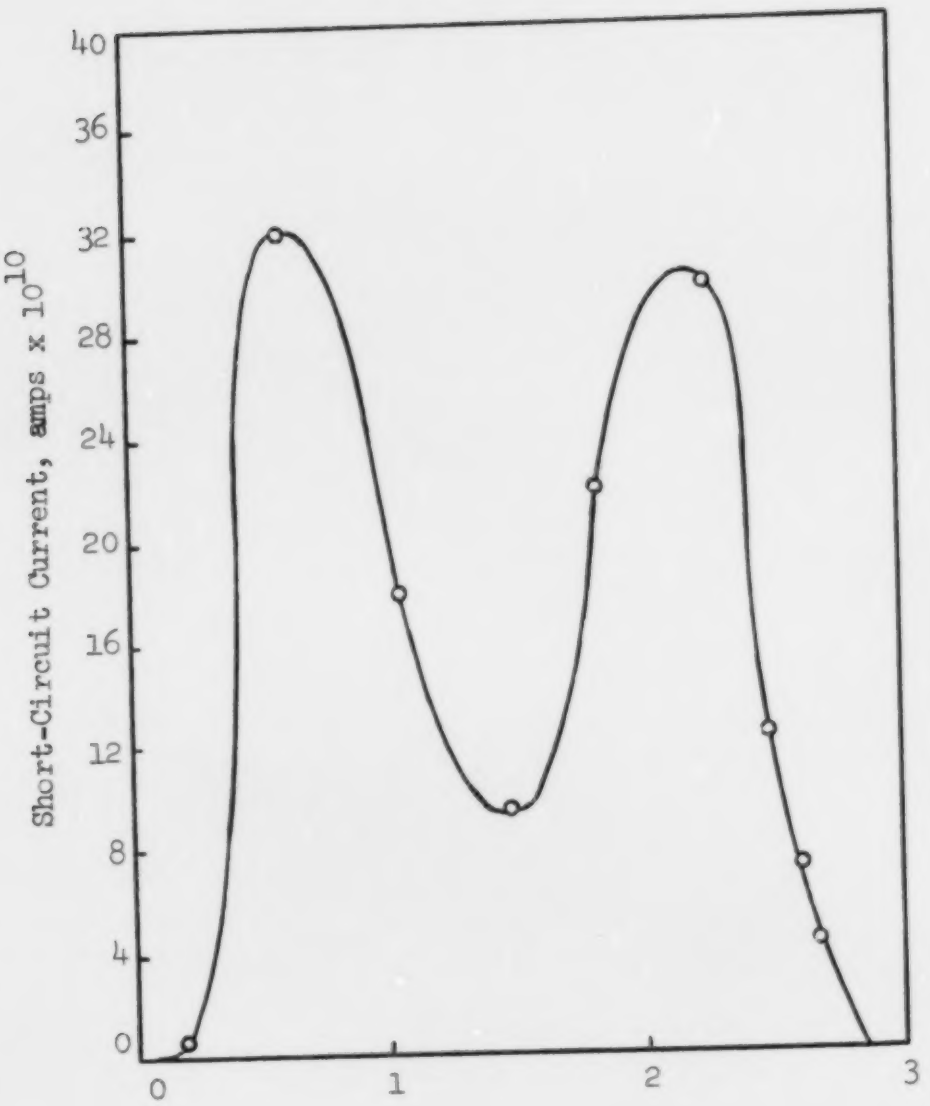

Figure 7. Short-Circuit Current Generated by Platinum on Fused Silica as a Function of Layers of Adsorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

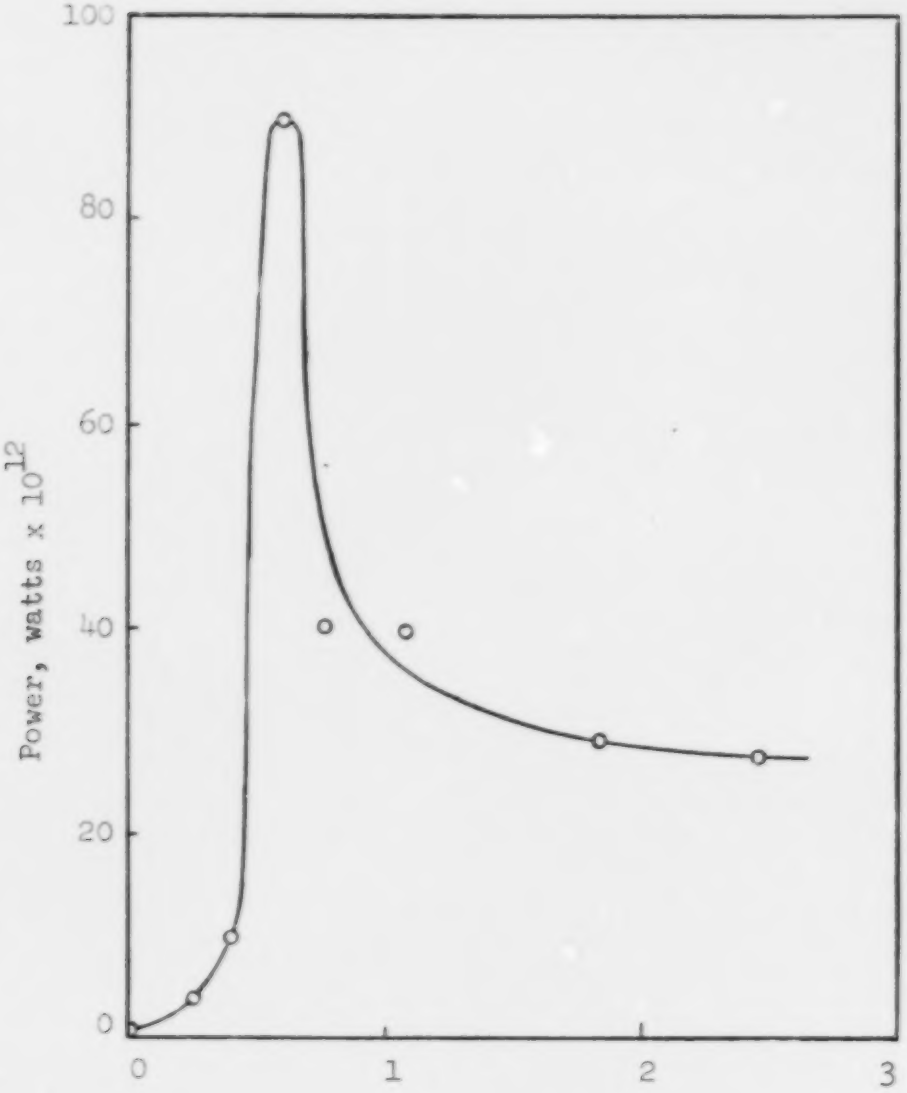

Figure 8. Power Dissipated Across a 2.5 x 10^6 Ohm Resistance by Platinum on Fused Silica as a Function of Layers of Adsorbed Water (Input Impedence, 10^{14} ohms; Rotation, 1200 rpm; Temperature, 25°C).

glass, Nylon, sulfur, Teflon, and polyethylene. The frictional charging of sulfur was relatively low (approximately + 0.6v), and remained essentially constant regardless of the water vapor pressure. This potential remained even without frictional motion. The system would again develop approximately + 0.6v when the platinum contact was shorted to ground and the ground connection was broken. The data for the charging of silica glass and Nylon at a rotational rate of 180 rpm are given in Figures 9 and 10. As shown, these materials developed relatively high charges in the presence of small quantities of water vapor. Teflon and polyethylene would only charge after the surface had been contaminated, for example, with fingerprints.

These experiments involving electrostatic charging as a function of the partial pressure of water showed again that sorbed water vapor is a primary cause of electrostatic charging. These data, together with the adsorption and sorption data, reveal that electricity was generated most readily when the water layer averaged only a few molecules thick. The data presented as short-circuit current suggest that charge generation is not due to a capacitive regeneration effect, since the platinum wiper (electrode) remained electrically near ground potential in this experiment and could not, therefore, induce significant quantities of charge on the rotating substrate.

The data given as power dissipated across a 2.5×10^6 ohm resistor, Figures 5 and 8, were obtained in order to convey an idea of the magnitude of the energy involved. Obviously, little electrical energy is created.

E. The Effects of Temperature

To determine the influence of temperature, all valves and lines of

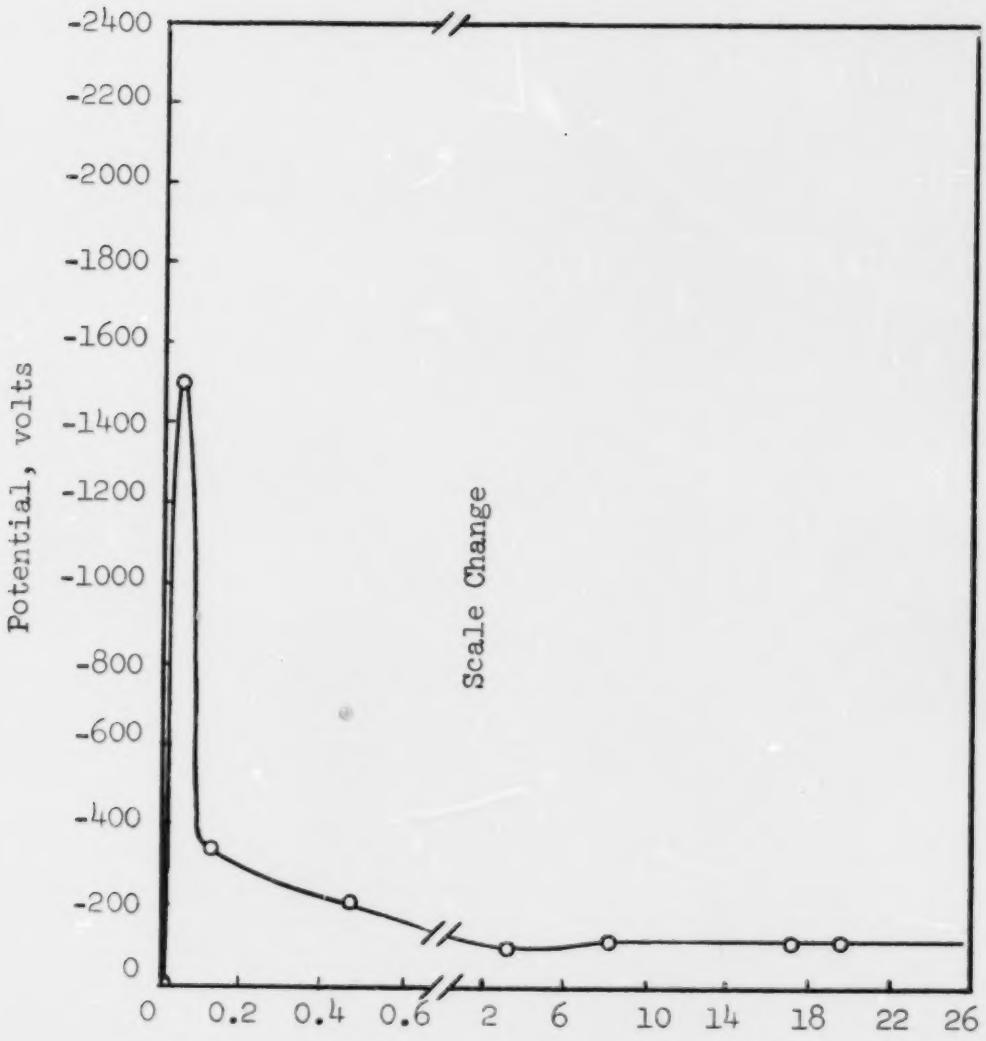

Figure 9. Electrostatic Voltage Generated by Friction Between Platinum and Silica Glass as a Function of Water Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

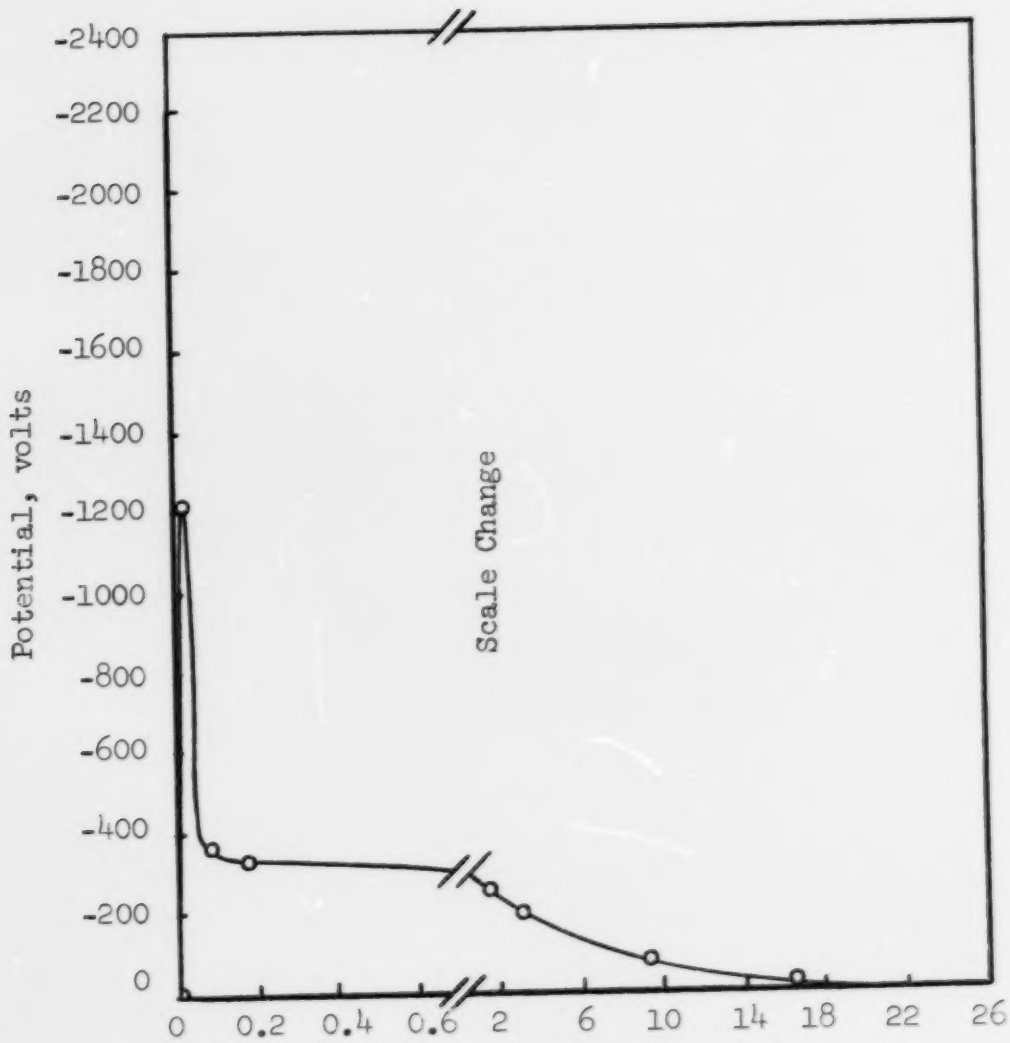

Figure 10. Electrostatic Voltage Generated by Friction Between Platinum and Nylon as a Function of Water Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

the apparatus described above were fitted for temperature control. A water holder was also attached to the entrance line and fitted so that its temperature could be measured and controlled. The water vapor pressure inside the apparatus was adjusted by regulating the temperature of the liquid water. The effect of temperature on the charging of sodium chloride at a rotational rate of 180 rpm as a function of relative pressure, i.e., the ratio of the actual pressure to the saturation vapor pressure of water, is shown in Figure 11.

The data clearly indicate that, in the case of NaCl, temperature, as well as the relative pressure of the water, alters electrostatic charging. Previously given results show that at maximum charging a thin layer of water vapor has been sorbed on the charging surfaces. Studies reported in the literature[3] indicate that near 30°C sorbed water exhibits a maximum density. It is suspected that a region of maximum density corresponds to a condition of maximum water molecule orientation.

F. Pure Gases and Their Influence on Electrostatic Charging

The influence of N_2O, CH_3CH_2OH, CH_3COCH_3, NH_3, and HCl were separately measured on a sodium chloride substrate at a rotational rate of 180 rpm. Of these, N_2O and NH_3 exerted only a slight influence on the charging, and the remainder showed no influence at all. Pieces of Teflon and polyethylene showed no charging in the presence of any of these gases. On all materials tested, except silica glass and Nylon, these gases seemed to have at most only a slight influence. The influence of HCl, NH_3, and N_2O on silica glass is shown in Figures 12, 13, and 14, and the influence of SO_2 and N_2O on Nylon is shown in Figures 15 and 16.

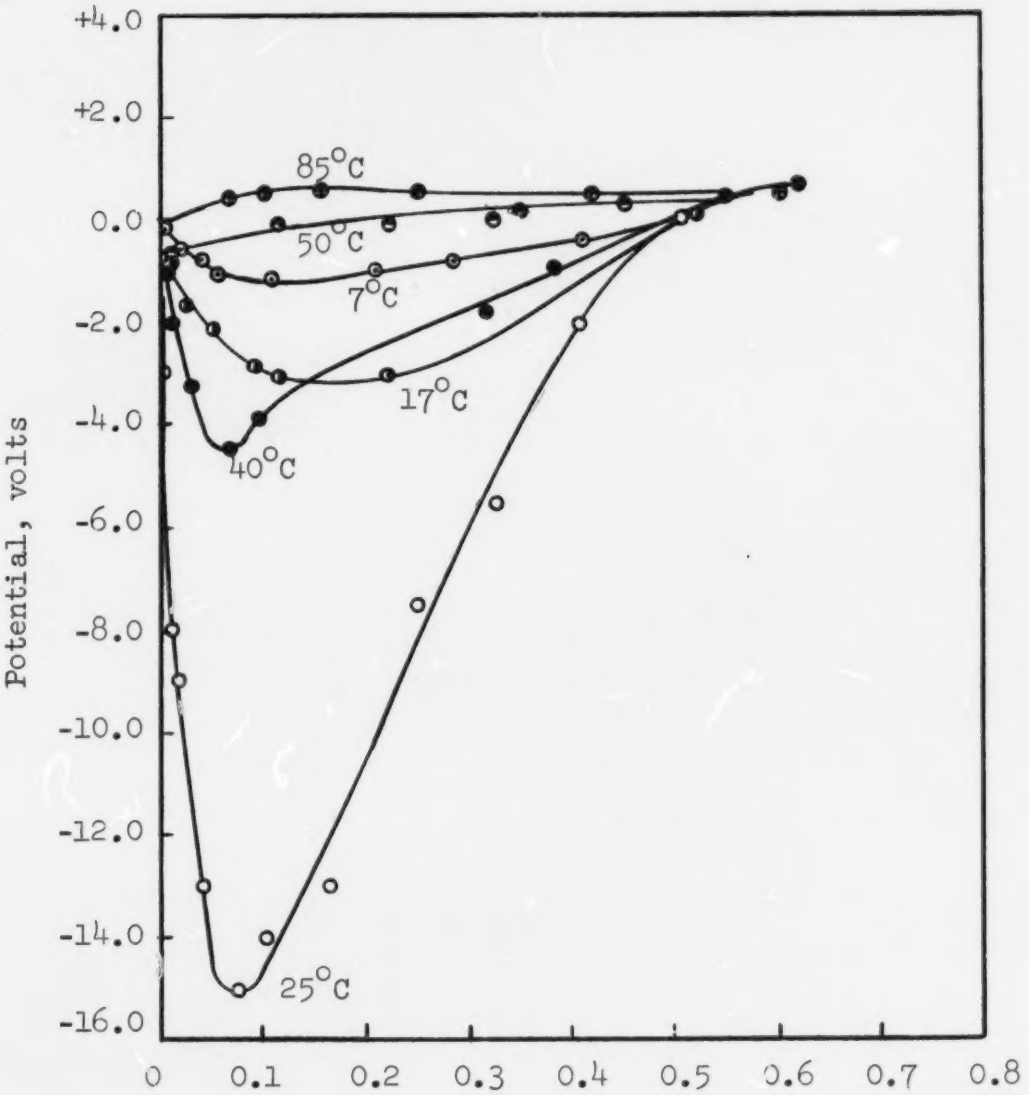

Figure 11. Potential Generated by Platinum on Sodium Chloride as a Function of the Relative Pressure of Water and Temperature (Input Impedence, 10^{14} ohms; Rotation, 180 rpm; Temperature, 25°C).

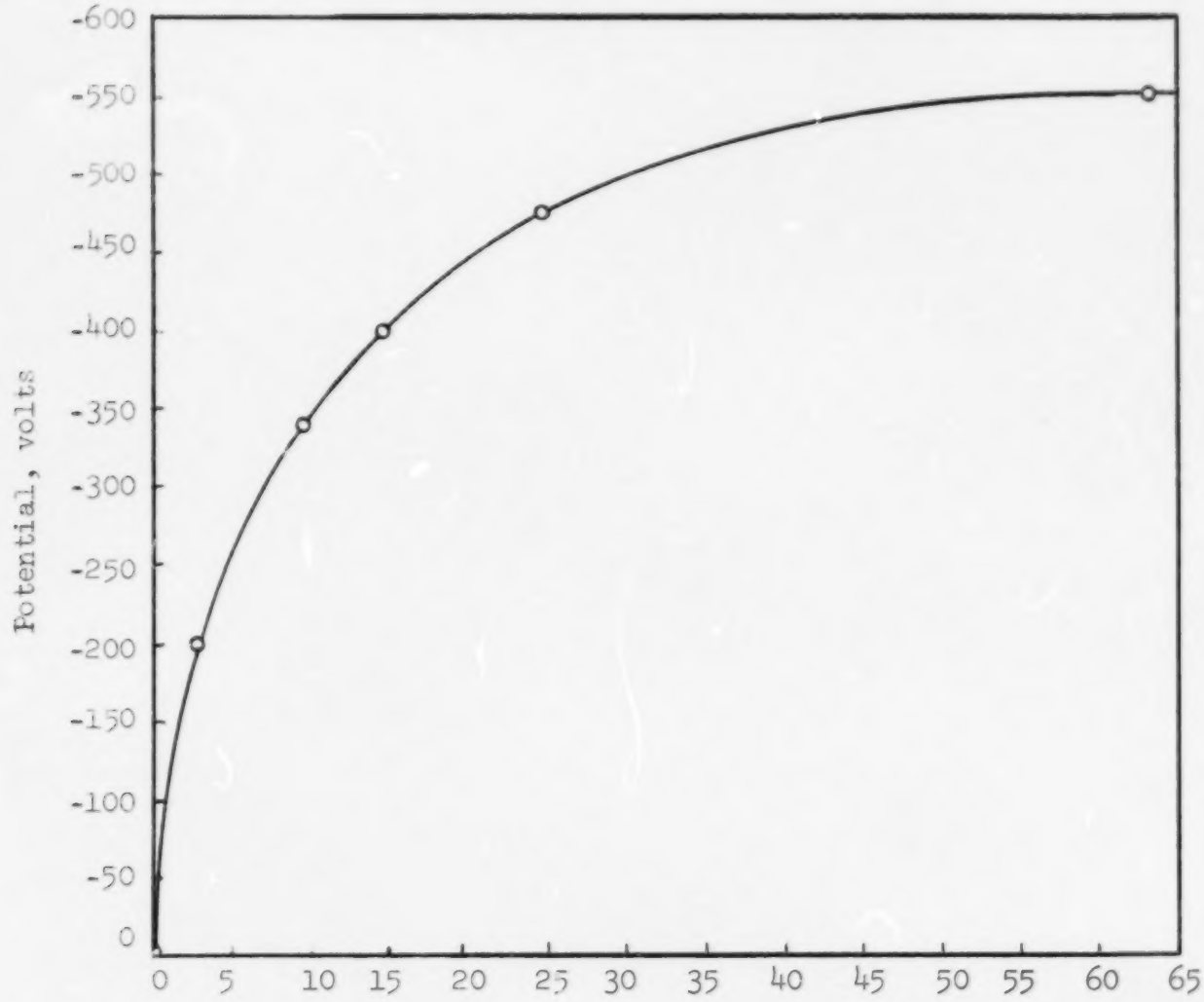

Figure 12. Electrostatic Voltage Generated by Friction Between Platinum and Silica Glass as a Function of HCl Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

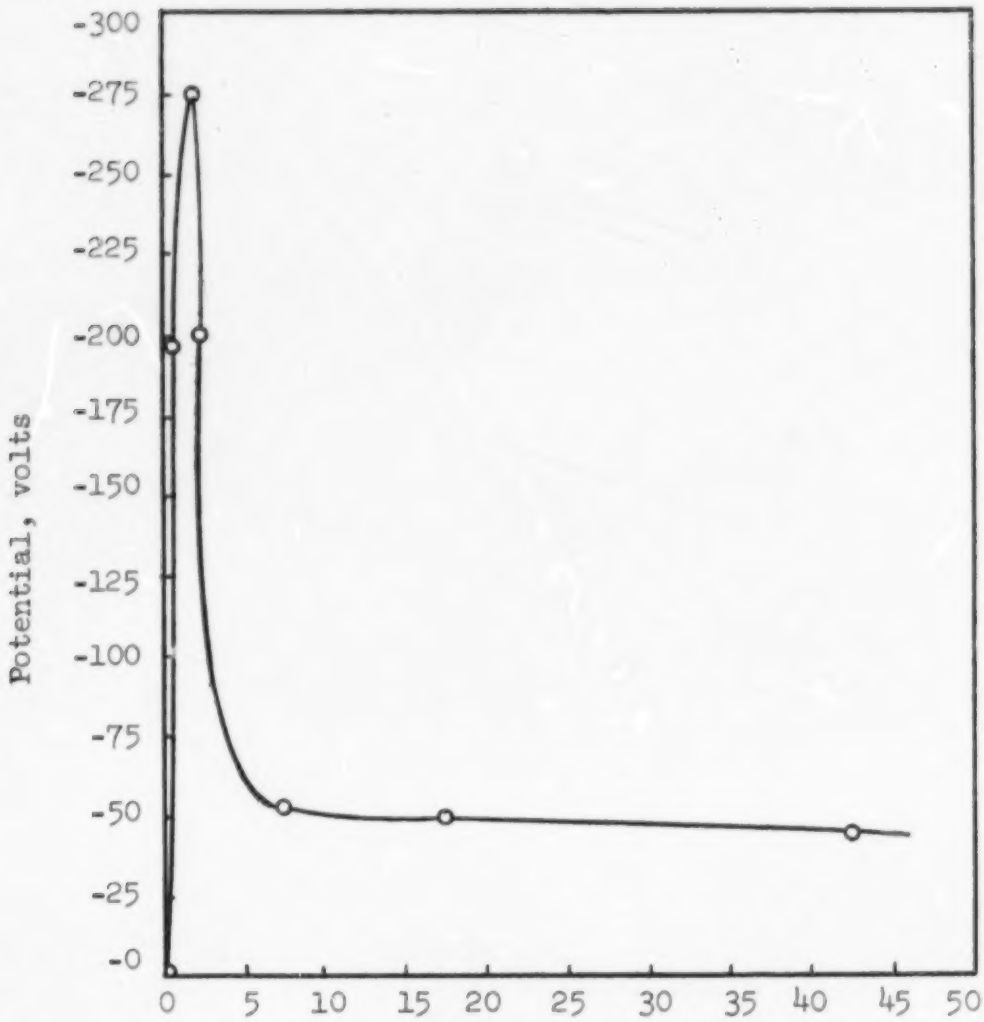

Figure 13. Electrostatic Voltage Generated by Friction Between Platinum and Silica Glass as a Function of NH_3 Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

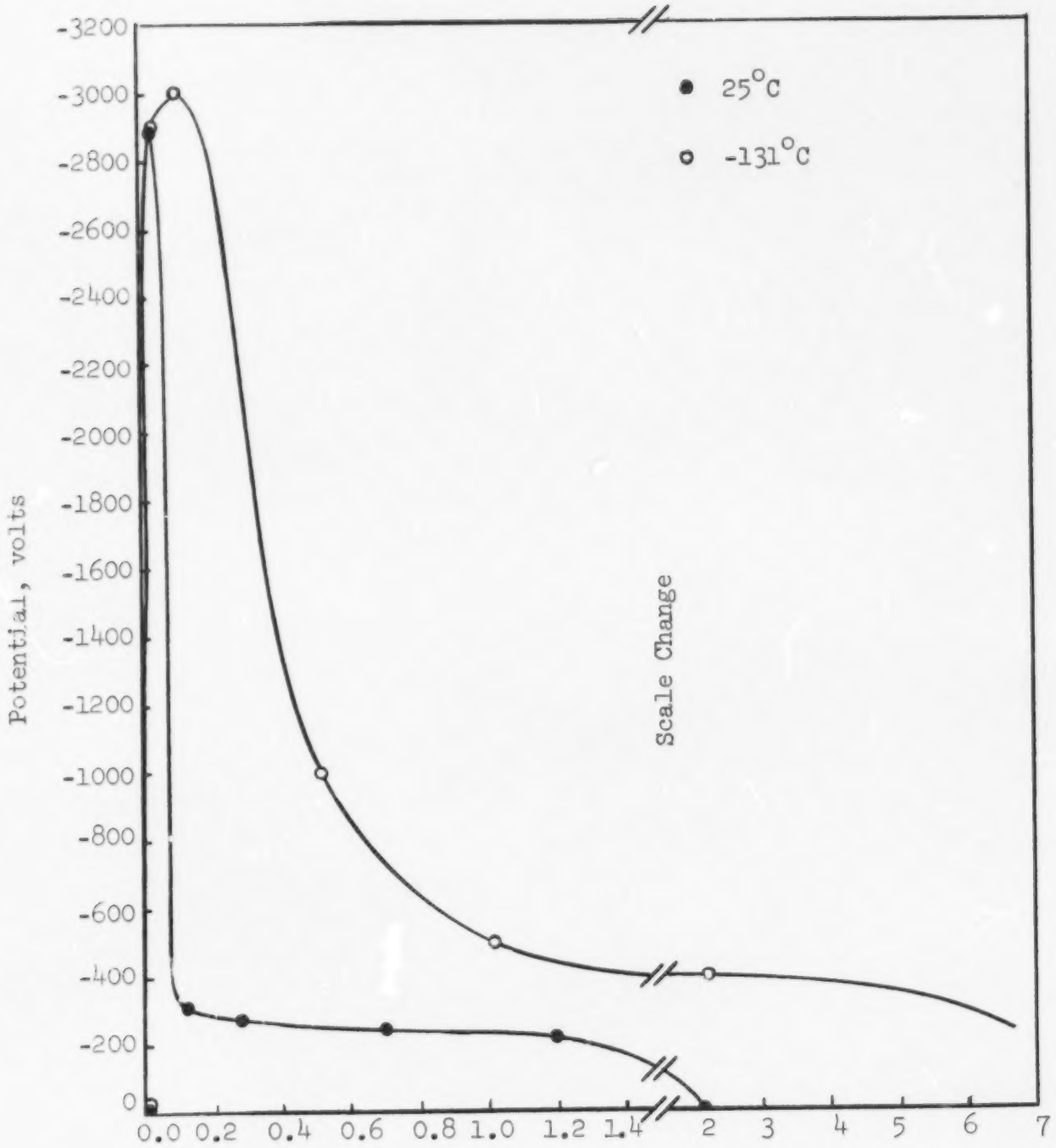

Figure 14. Electrostatic Voltage Generated by Friction Between Platinum and Silica Glass as a Function of N_2O Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180^2 rpm).

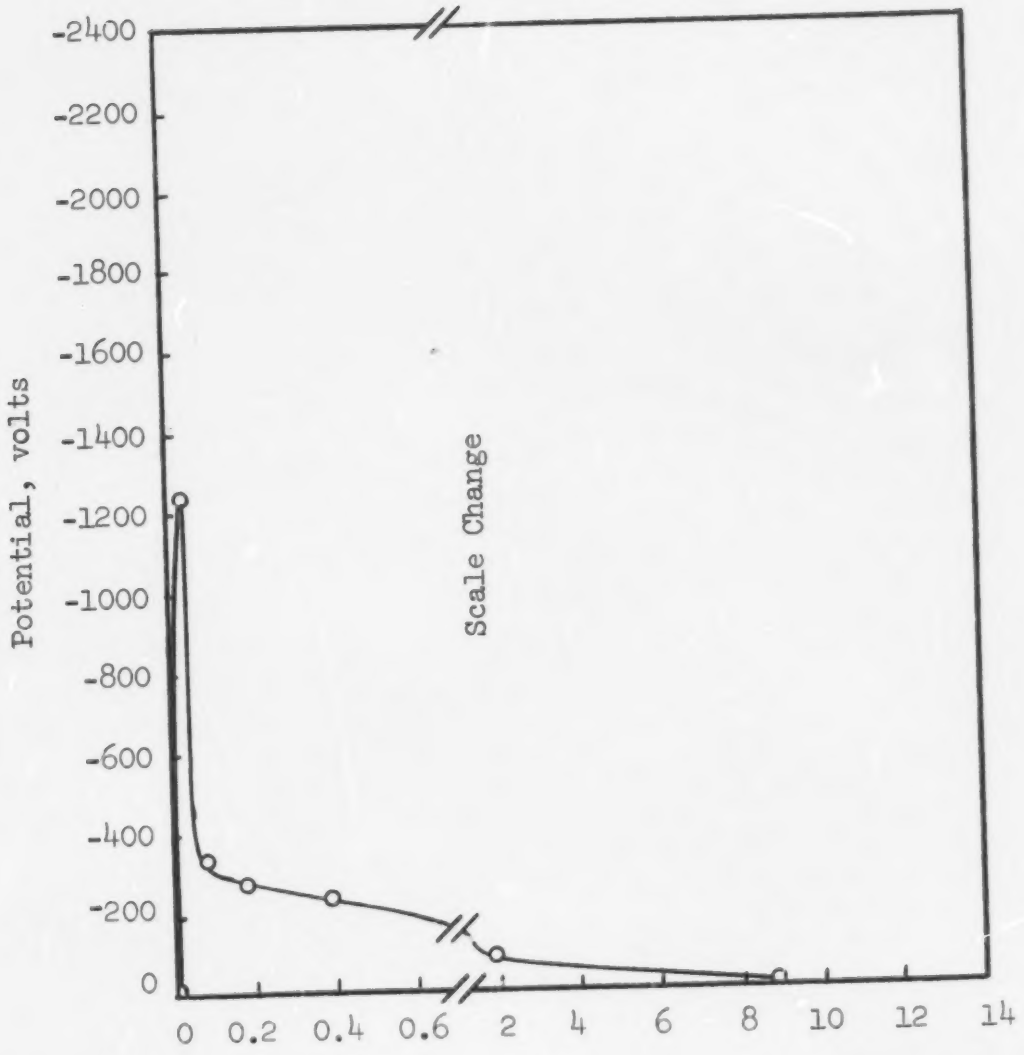

Figure 15. Electrostatic Voltage Generated by Friction Between Platinum and Nylon as a Function of SO_2 Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

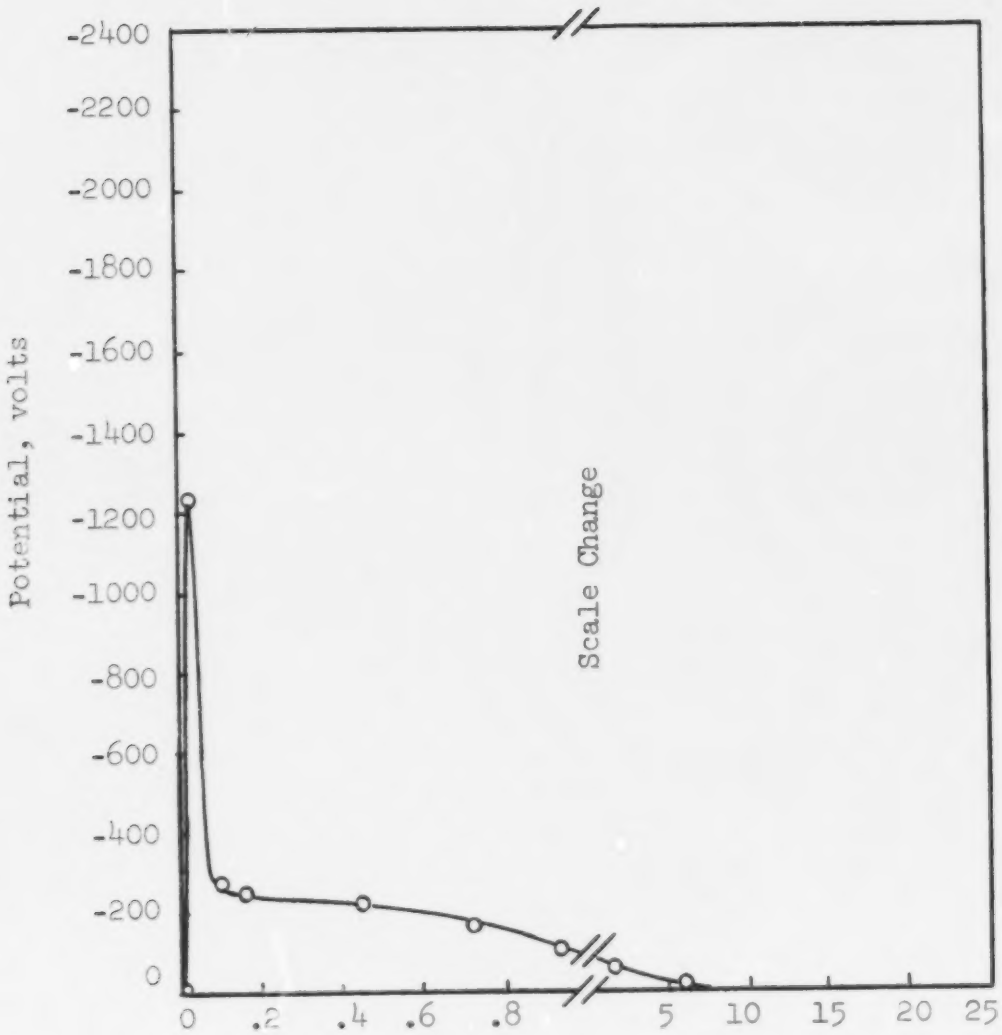

Figure 16. Electrostatic Voltage Generated by Friction Between Platinum and Nylon as a Function of N_2O Vapor Pressure (Input Impedence, 10^{11} ohms; Rotation, 180 rpm; Temperature, 25°C).

Why only SO_2, NO_2, HCl, and NH_3 should affect the charging of silica glass and Nylon is not known. However, adsorbed water is extremely difficult to remove from both materials. Water is reported[4] to chemisorb on silica glass. Nylon is extremely difficult to outgas, and there is doubt that it can be completely outgassed.

G. Effects of N_2O on Electrostatic Charging at Reduced Temperature

Since multilayer adsorption of many of the above gases on a solid surface could only be attained at room temperature at a pressure beyond the capabilities of the system, the apparatus was altered again to accommodate low temperatures where sufficient adsorption could be achieved at relatively low pressure. To accomplish this the bath about the apparatus was insulated and a coil of copper tubing was placed inside the tank but outside the bell jar. One end of the tube was connected to a cylinder of liquid nitrogen and the other was left open. The tank was filled with n-pentane. By controlling the liquid nitrogen rate of flow and stirring the n-pentane, the n-pentane could be kept in a semisolid state[5]. This gave rather constant temperature conditions at the melting point of n-pentane, viz., -131°C. Results of experiments with N_2O gas and silica glass at this lower temperature and a rotational rate of 180 rpm are given in Figure 14.

This experiment was designed to produce multilayer adsorption of N_2O on the silica surface in order to determine the influence of an adsorbed multilayer other than water. A peak in the generated voltage at low relative pressure was found very similar to the peak at room temperature. However, at -131°C the voltage was greater and remained so even at high relative

pressures. At room temperature the voltage returned to zero as the pressure increased. These data indicate that frictional charging is enhanced when conditions are such that enhanced adsorption can occur.

V. DISCUSSION OF RESULTS

A. Apparatus

While 10^{14} ohms, the resistance of the electrometer of this study, or 10^{11} ohms, the resistance of the electrometer when employing the high voltage probe, is a high input impedence, it still permits a current drain and must be considered in any discussion of results. Also all substrates, except graphite and silica glass, showed resistances of the order of 10^{8} to 10^{9} ohms. Silica glass presented a resistance in excess of 10^{11} ohms while the resistance of the graphite was extremely low. This means that, in actuality, current flow was primarily the parameter measured, and that the voltage actually generated with no load may be slightly greater than reported herein. There are electrometers that can measure the electrostatic charges on a surface without loss, however none could be found that would permit measurements inside a vacuum chamber. This latter capability for the apparatus was most important in this study. While the current drain of the electrometer employed may have altered slightly the absolute voltages given, general trends in charging should be representative.

B. Samples

Surface conditions are of extreme importance in any analysis of electrostatic charging. The cleaning and outgassing procedures employed should have made all solid surfaces reasonably representative. In general, this was borne out by the fact that the data presented were in most instances quite reproducible. However, since all surfaces, including the platinum, were subject to a sliding motion, wear did occur, and surface

states may have been altered after testing was begun. The fused silica was very abrasive and after a few hours of testing its surface became gray due to accummulated platinum particles embedded in its pores. After many hours of testing the silica glass showed no signs of wear and the platinum showed only a few minor scratches. The polymers showed no signs of wear. Specimens, such as sodium chloride, that had been pressed into a compact mass disintegrated slightly under friction and produced a fine powder deposit which became evident on the bottom of the apparatus after extended use.

C. Charging Results

A dynamic system such as investigated in this study leads inevitably to results that are somewhat erratic. In general, electric noise was encountered until a monolayer of adsorbed gas was established. At this point the output became very constant. To obtain a value for the charging when the signal was erratic, the output, as recorded, was visually averaged. The noise component was as high as 50 volts peak-to-peak when electrostatic charging was most erratic and high charges were being developed. This may have been due to periodic cold welding of the platinum to the solid against which it was rubbing followed by weld breaking and particle production. When dry air, for example, was admitted to the bell jar, voltage generation became quite stable although near zero in most cases. Air is well known as a lubricant for surfaces because it retards cold welding.

VI. CONCLUSIONS

According to contact potential theory[6], an electrical double layer[7] [8] [9] is formed when two dissimilar materials are placed in contact, the double layer often incorporating the Fermi level of the surface atoms of the substances involved. Dissimilar materials thus behave very much as do thermocouples composed of metals. This type of behavior probably accounts for potentials of one volt or less and is probably the mechanism involved in the charging of sulfur, for example, as reported herein. However, charging of this magnitude would have been masked in much of this study by electrical noise, particularly at low gas pressures where it should have been most important. The electrometer as employed did not lend itself to measuring extremely low voltages, and many measurements fluctuated too much for very low potentials to be detected accurately. Contact potential theory does not explain the high potentials or why the high voltages disappear when friction stops. No friction is required by this theory. Also this concept does not account for the effects of adsorbed gases on the surface of materials. One exponent of this theory[8] showed that as the humidity increased the surface conductivity increased and that the breakdown potential of the gas medium decreased with increasing water vapor pressure. While this is apparently true, resistivity measurements for the apparatus of this study showed that, on all materials except silica and graphite, the total system resistance was in the range of 10^8 to 10^9 ohms and that very little change occurred in this resistance where charging variations were pronounced. Resistances generally remained within the same order of magnitude even though potentials varied several orders of magnitude.

In a related study[7,8], outgassing a silica ball to a high vacuum in a system constructed of nickel around which the ball rolled resulted in decreased charging just as was found in this investigation. The decrease was attributed to contamination of the silica surface by the nickel. This conclusion cannot be ruled out completely but it seems extremely doubtful. In another study[10] electrostatic charging of materials such as CdS and Zr was correlated with different types of light radiation. No details were given of pressure, humidity, or gas content of the ambient atmosphere. Related experiments of this study using selenium under vacuum indicated that light radiation had no effect. It would seem quite possible that in the earlier study the light energy served to cause adsorbed vapor evaporation which would clearly alter the charging.

Another theory involves chemical reactions which are catalyzed by friction.[12] Exponents of this theory maintain that friction causes adsorbed gases, such as water vapor, to ionize and to react with one of the solids giving up or gaining electrons. The theory is not in conflict with the described influence of water vapor except that it does not account for the drastic decrease in potential observed with a slight increase in adsorption and the unusual effects of temperature. If the causes of electrostatic electricity were chemical in nature, different relationships should be expected.

Among the theories suggested to describe electrostatic charging, in the presence of water, one of obvious importance involves ion transfer. Dielectric liquids are accompanied by an electrical double layer (the Stern-Gouy layer) at a solid-liquid interface.[11] As a consequence, disruption of such a liquid layer by mechanical means, including friction, might be

expected to give rise to charge separation. Most of the charging found in this investigation was developed under conditions such that this double layer was unlikely to have been well developed. Therefore, its disruption is not believed to have been of great significance.

Results of this study show that dielectric liquids (water and, to a lesser extent, N_2O) cause quite extensive charging. Studies employing pulsed N.M.R.[13] and other means[3] have shown that the first layer of adsorbed water on a solid is well oriented and that this orientation diminishes to the properties of bulk water as the number of layers increases. Adsorbed water molecules next to a surface aligned with the hydrogen atoms attached to the surface[3]; they thus exhibit all the characteristics needed to produce a piezoelectric effect. Any force on a surface covered with a layer of adsorbed water molecules would be applied along the axis of their dipole moment. As with piezoelectric solids, this force would be expected to cause a flow of electrons from the negative end of the dipolar molecule to the positive.

Friction between two seemingly flat plates takes place actually only between the high points of each plate, therefore electrical contact with each high point is broken at the same time as the force is released. When force is released slowly from a piezoelectric material the charge across it returns to zero, but some of the charge generated remains on the force applicator if contact is broken rapidly. When this process is carried out by a rapid, sliding motion, as it would be with the apparatus employed here, the result would be a flow of electrons, passing from the platinum wiper, through the electrometer, through the ground to the apparatus, and to the other solid surface. With the exception of fused silica, all solids

gave a negative charge as this mechanism would require. Piezoelectricity is thus believed to be a significant factor in tribo electrification under a great many circumstances.

The fused silica was the least pure, most abrasive, and most porous of all materials studied. Charging of it may have been dictated by a mechanism, or combination of mechanisms, different from those described.

All data of this study indicate that adsorbed water vapor is the main cause of electrostatic charging and that maximum charging occurs at conditions giving a layer of adsorbed (or sorbed) water only a very few molecules thick.

In general, other gases influence charging when the materials in contact are exposed to the atmosphere by altering the adsorbed water layer. No evidence was found of a pollutant gas that caused a significant increase in the absolute voltage generated; vapor of HCl decreased the charging in some instances to zero, possibly because of increasing the film conductivity.

Materials such as Teflon and polyethylene which do not readily adsorb water on their surface generate little frictional electricity. Charging occurs, however, when the surface of these materials is contaminated with another substance that enhances water adsorption.

It is concluded that frictional electrostatic charging as normally encountered under atmospheric exposure is most often the result of a distortion of oriented water molecules adsorbed on the surface of solids, i.e., at conditions of intermediate relative humidity. The disruption of the Stern-Gouy layer and the transfer of ions possibly becomes of importance as the molecular layers increase with increasing humidity. At high humidity, the layer either becomes disordered or sufficiently thick and conducting to

short-circuit the generation process. Less polar molecules, such as N_2O, behave in a similar, although less vigorous, manner when adsorbed in sufficient quantity. Low temperature and high pressure enhance the adsorption of the more volatile gases. Pollutant gases are generally ineffectual because they are little adsorbed by solids exposed to the atmosphere due to the preferential adsorption of water vapor.

Respectively submitted:

Clyde Orr, Jr.

Clyde Orr, Jr.
Project Director

Approved:

M W Long for

Frederick Bellinger, Chief
Chemical Science and Materials Division

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